



Electrodeposited lead-foam grids on copper-foam substrates as positive current collectors for lead-acid batteries



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HIGHLIGHTS

- Lead (alloy) foam was prepared by electrodepositing lead on a copper-foam substrate.
- Lead foam was used as a positive current collector for lead-acid battery.
- The thick lead coating protects the copper substrate against corrosion.
- Lead foam electrodes have a low current density and internal resistance.
- The 3D net structure lowers the shedding rate of active materials.

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ABSTRACT

Contemporary lead-acid batteries have a high internal resistance and a limited utilization of their positive active materials (PAM). In order to alleviate these problems, lead (alloy) foam-based positive electrodes for lead-acid batteries are prepared by electrodepositing lead on a copper-foam substrate. Using scanning electron microscopy, flame atomic absorption spectrometry, finite element analysis, cyclic voltammetry, and galvanostatic charge/discharge tests, the effect of the lead foam collectors on the electrochemical performance of the positive electrodes is characterized. The thickness of the lead coating has a strong effect on the corrosion-stability of the copper-foam substrate. In addition, the charge/discharge performance of the batteries is greatly improved by the lead-foam collectors. At the 20–2 h discharge rates, the utilization efficiency of the PAM of 40-PPI lead-foam battery is improved by 19–36% from the cast-grid battery. Combined with the finite element analysis, it appears that the 3D connected network structure of the positive lead foam electrode can reduce the surface current density, the polarization resistance, and the ohmic resistance of the battery because of its larger contact area with the active material. As a result, the lead foam battery has a higher utilization efficiency of the PAM.

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1. Introduction

The lead-acid battery is the most ubiquitous energy storage device and its extensive list of applications includes electrical power supply for automobiles, communications, and railways. Although its specific capacity is low and deep cycle life is short as compared to the lithium battery or the nickel-hydrogen battery, its good power characteristics, small self-discharge property, excellent high and low temperature performance, sophisticated production process, recyclability and cost-effectiveness, have enabled it to be the current mainstream of secondary batteries [1,2].

Lead-acid battery conventionally has a low specific capacity because of its heavy weight [3–5], which is concentrated predominantly on the lead grid and the active material. In order to improve the energy density and reduce the weight of a lead-acid battery, a substantial amount of work has been done to optimize the structure of the collector grid [6–12] and the composition of the active material [13–17]. Of the various ideas proposed, the substitution of the conventional cast grid with a porous lead-foam grid having a high specific surface area seems to be an efficient method to improve the utilization efficiency of the active material in a lead-acid battery [18–20]. There are several reports on the development of foam-based electrodes for batteries, especially reticulated vitreous carbon (RVC) foams, which are usually coated with lead and then used as a current collector for lead-acid batteries [21–25]. However, these materials have limited use as positive current collectors because they face problems such as oxygen evolution [26],

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degradation of bond strength and corrosion of the coating [27]. On the other hand, copper foam, which has an excellent electrical conductivity, has also received increased attention in recent years as a current collector for lead-acid batteries. Tabaatabaai et al. [28] had prepared open cell lead foams by electrodeposition of lead alloy onto copper foam substrates. These lead-foam grids were used as the negative current collectors in batteries, which showed 42% increase in their specific capacity over their standard forms. This improvement was attributed to the high conductivity of the lead-foam grid structure, which was promoted by copper and the high utilization of the active material due to the optimized three-dimensional structure of the collector. Dai et al. [29,30] also employed a lead-foam grid as the negative current collector of a lead-acid battery, and studied its effects on the battery performance. Their results showed that the lead-foam grid had a larger specific surface area than the conventional cast grid. In addition, the charge voltage of the battery having a lead-foam negative electrode was much lower than that having a cast grid electrode during the charging process. Moreover, the discharge capacity, mass specific capacity, and the active material utilization efficiency of the battery having the lead-foam electrode were greatly improved over that having the cast grid electrode at different discharge states. Yolshina et al. [31,32] had investigated lead-film electrodes on copper, aluminum and copper-coated titanium substrates. They concluded that in a lead coated copper grid electrode, the leaching of copper ions into the acid electrolyte through the pores in the lead coating was hampered by the higher positive standard potential of the electrode; and the lead-covered copper grid can be used as the positive current collector in lead-acid batteries as they allow high values of discharge current density to be obtained. Though there are several studies on lead foams used as negative current collectors, there are few reports on the use of lead foams on copper substrates as positive current collectors in lead-acid batteries. The lead (alloy) foams as positive current collectors are supposed to reduce the internal resistance of the battery to improve the utilization of the active materials at the positive electrode.

In this paper, lead-foam grids with different pore densities were successfully prepared by the electrodeposition of lead on a copper-foam substrate. These lead foam grids were fabricated as the positive electrodes of lead-acid batteries after the pasting, solidification and forming processes. Their performance in an experimental battery was investigated by the means of scanning electron microscope (SEM), cyclic voltammetry, and galvanostatic charge/discharge tests.

2. Experimental

2.1. Preparation of the lead foam

5 mm thick polyurethane (PU) foams (Changzhou Daye Tengfei Sponge Factory, China) having 20 and 40 pores per inch (PPI) as shown in Fig. 1a, were used as the precursor phase structure.

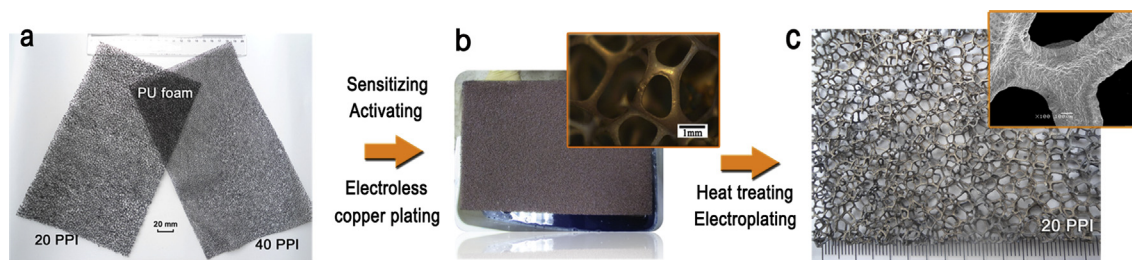


Fig. 1. Preparation of the lead foam: (a) PU foam of 20 and 40 PPI, (b) electroless copper plating, and (c) lead electroplating process.

Table 1

The technological parameters of copper electroless plating and lead electroplating.

Copper electroless plating		Lead electroplating	
Reagent	Dosage (g L ⁻¹)	Reagent	Dosage (g L ⁻¹)
CuSO ₄ ·5H ₂ O	20	HF (40%)	300
HCHO (37%)	40	H ₃ BO ₃	120
KNaC ₄ H ₄ O ₆	100	2PbCO ₃ ·Pb(OH) ₂	150
NaOH	12	Peptone	0.5
Na ₂ CO ₃	3	—	—
MBT	Trace amount	—	—
Additives (1, 4-butyne diol, Polyethyleneglycol, NiCl ₂ etc.)	Trace amount	—	—
Temperature: 25–30 °C; pH: 12.5–13		Temperature: 18–30 °C; current density: 1–3 A dm ⁻² ; mechanical stirring	

Copper foams were prepared by first subjecting the PU foams through pre-treatment (sensitization and activation) followed by electroless copper plating and heat treatment (Fig. 1b). The copper foams were then used as substrates to prepare lead foams by the electroplating process (Fig. 1c). The electroplating process was conducted in a fluoroborate solution with the copper foam as the cathode, and a lead plate as the anode. The technological parameters of copper electroless plating and lead electroplating are presented in Table 1.

2.2. Electrochemical behavior of lead-foam electrode and lead cast grid electrode in sulfuric acid solution

To prepare the lead-foam electrode, the lead foam was cut into pieces of dimensions 25 × 25 × 5 mm³ and connected with copper conductors. The exposed copper conductors were wrapped with silica gel to prevent acid corrosion. For comparison, a lead cast grid was cut into pieces of dimensions 25 × 25 × 1 mm³, which is almost as heavy as the lead foam of 25 × 25 × 5 mm³. The cast-grid electrode was prepared via the same method described above. The electrochemical behavior of these two electrodes was tested by cyclic voltammetry after they were deoiled and cleaned.

The cyclic voltammetry tests were carried out using a CHI660C electrochemical workstation (Shanghai CH Instrument Company, China), which was connected to the lead foam or lead cast grid set as the working electrode, a platinum sheet set as the counter electrode, and a Hg/Hg₂SO₄ electrode set as the reference electrode (Fig. 2). The electrolyte was a 4.8 M Hg₂SO₄ solution. The scanning rate was set as 20 mV s⁻¹ in the voltage range of −1.4–2.5 V. The tests were performed at room temperature.

2.3. Battery fabrication and charge/discharge test

Lead foams of 20 and 40 PPI were cut to the following dimensions 145 × 110 × 5 mm³ to constitute the current collectors.

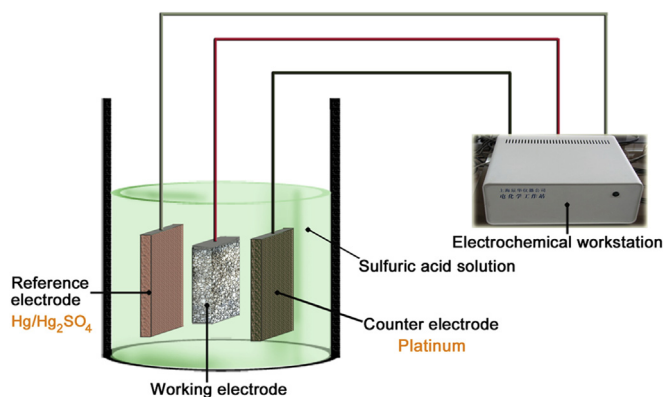


Fig. 2. Schematic of the cyclic voltammetry test setup.

Due to the porous structure of the foams, a lead sheet was welded at its edge to allow the attachment of connector to guarantee its conductivity (Fig. 3a). The lead-foam grid was fabricated as a positive electrode following the pasting, solidification, and formation processes (Fig. 3b). The positive and negative paste was provided as the common paste by Yangzhou Apollo Battery Co., Ltd. The positive paste consisted of lead oxide based powder, sulfuric acid, and distilled water, while the negative paste needed additional composition such as barium sulfate and lignosulfonate. The lead oxide based powder in the paste was composed of 75 wt% lead oxide and 25 wt% metallic lead. The paste was physically forced into the pores of foam with a wooden spatula, and excess paste was scraped off. Drops of acetone and water were added to reduce the viscosity of the paste so that it could completely penetrate the foam. The conventional lead cast grid electrode was prepared following the same procedure. The pasted samples were cured at 65 °C and a relative humidity 90% for about 36 h, and then dried at 80 °C for 12 h. The formation process was performed in 1.15 g cm⁻³ H₂SO₄ solution using a constant current method [19]. To form the battery the negative-positive-negative configuration was used, wherein the positive foam electrode was sandwiched by two lead cast grid set as the negative electrodes (Fig. 3c). The positive lead foam electrode was enclosed in a PVC bag to prevent direct contact with the negative electrodes. The electrolytic solution was a 4.8 M Hg₂SO₄ solution.

Table 2 shows the apparent density ρ , and the electrode design factors α and γ of the lead-foam grid-based and lead cast grid-based electrodes. α is the ratio of current collector to electrode weight ($\text{g}_{\text{COL}} \cdot \text{g}_{\text{ELECTRO}}^{-1}$), and γ is the ratio of the active mass to the collector surface area ($\text{g}_{\text{AM}} \cdot \text{cm}_{\text{COL}}^{-2}$). From the table it can be seen that the apparent collector density ρ and the design factor α of the lead-foam positive electrode were reduced only slightly, while the

Table 2

Physical characteristics of the lead-foam and the conventional lead cast grid electrodes.

Electrode	$\rho (\text{g}_{\text{COL}} \cdot \text{cm}_{\text{COL}}^{-3})$	$\alpha (\text{g}_{\text{COL}} \cdot \text{g}_{\text{ELECTRO}}^{-1})$	$\gamma (\text{g}_{\text{AM}} \cdot \text{cm}_{\text{COL}}^{-2})$	Equivalent mass of PAM (g)
Cast grid	2.21	0.35	2.48	348
Lead foam (20 PPI)	1.16	0.25	0.07	305
Lead foam (40 PPI)	1.84	0.34	0.04	332

design factor γ was reduced by more than an order of magnitude in comparison to the lead cast grid positive electrode. To better understand these factors, the equivalent mass of PAM for the three electrodes is also shown in Table 2. The equivalent mass of PAM is defined as the actual mass of PAM in the positive electrode with dimensions of 145 × 110 × 5 mm³. Influenced by filling method the viscosity of paste in the preparation process, the lead foam can be filled with slightly less PAM than the cast grid per unit volume. 40-PPI lead foam can be filled with more active materials than 20-PPI one at the same apparent volume. This implies that the lead foam has a significantly greater contact area but a slightly lower weight in comparison to the lead cast grid, which leads to an enhanced utilization of the active materials of the batteries.

The charge and discharge performances were evaluated according to the industry standard mechanism of the People's Republic of China (JB/T 10262-2001) for sealed lead-acid batteries used in an electric moped. A battery performance tester (BTS 5V/10A, Neware Technology Company, Shenzhen, China) was used to draw/supply a constant current for discharging/charging the experimental batteries and also to monitor the changes in voltage during the process of charging and discharging. The charge currents used were 0.5 A and 2 A, and charging was assumed to be completed when the voltage of the battery was stable (2–3 h). Discharging of the batteries was done using constant currents at the 20 h rate (I_{20}), 10 h rate (I_{10}), 5 h rate (I_5), 2 h rate (I_2), and it was assumed to be completed when the voltage dropped to 1.6 V. The leaching of copper ions into the sulfuric acid solution was monitored by a TAS-990 atomic absorption spectrophotometer (Beijing Purkinge General Instrument Co. Ltd., Beijing, China). The measurement was carried out in an air-acetylene flame. Copper hollow cathode lamps were used as the radiation source at the wavelengths of 324.8 nm, with a current of 3.0 mA and a 0.4 nm slit width.

3. Results and discussions

3.1. Morphology of the lead foam

Fig. 4a and b show SEM images of the copper-foam grid before and after heat treatment. The copper particles plated on PU by

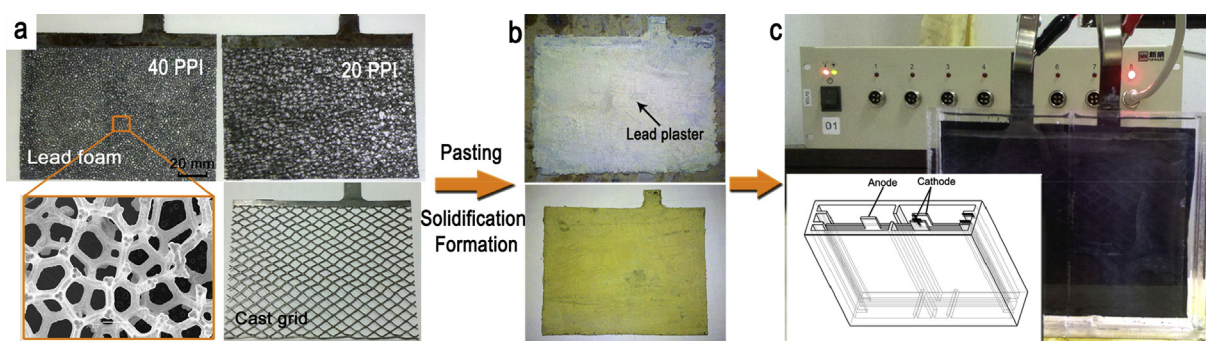


Fig. 3. (a) Images showing the morphology of the lead-foam and conventional lead cast grid; (b) Pasting, solidification and formation processes for preparing the lead-foam positive electrode; (c) performance-measurement system for the batteries in the negative-positive-negative configuration.

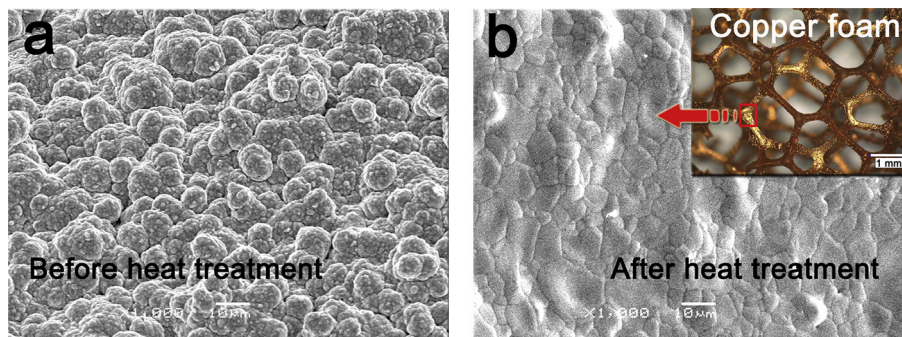


Fig. 4. Morphology of the copper-foam surface (a) before and (b) after the heat treatment process; the inset showing the optical micrograph of the copper foam after the heat treatment process.

electroless copper deposition appeared to make the copper-foam surface rough before the heat treatment process (Fig. 4a). The rough surface of the copper foam makes it difficult to get an optimum coverage of lead during the lead electroplating process. In addition, if areas of the copper-foam substrate are exposed to the electrolyte due to insufficient coverage of lead then oxygen evolution reactions occur hindering the electrochemical reactions of PAM and gradually corroding the inner copper during charge/discharge cycles. Therefore, to make sure that the copper foam was protected by a uniform, dense, and complete coverage of lead, heat treatment was carried out to make the surface of the copper foam smooth (Fig. 4b). Fig. 5 presents an optical image of a representative cross-section of the electroplated lead foam. The image shows that the electrodeposited lead has good contact with the copper-foam substrate. The thickness of the lead coating was about 117 μm , which was approximately three times the thickness of the copper layer. A minimum thickness of the lead coating layer in the lead foam is essential because positive current collectors are likely to be corroded during charge/discharge cycles. A thick lead coating will supposedly protect the copper-foam substrate against damage by electrolyte penetration or leaching of copper.

3.2. Voltammetric behavior of the electrode in sulfuric acid

Cyclic voltammetry was performed to determine a wide range of electrochemical information of the lead foam and conventional

cast-grid-based electrodes. Fig. 6a shows single-cyclic voltammograms of the lead-foam collector (40 PPI) and the conventional lead cast grid collector in sulfuric acid at the third cycle. As expected, there were two oxidation peaks A_1 and A_3 during the anodic scan, and four deoxidization peaks C_1 , C_2 , C_3 , and C_4 during the cathodic scan. Based on the electrode potentials, peak A_1 corresponds to the oxidation peak of Pb, in particular to the generation of PbSO_4 . Along with the PbSO_4 film a layer of PbO is also generated simultaneously under the PbSO_4 film. The sub-layer of PbO can prevent SO_4^{2-} and HSO_4^- ions from penetrating into the inner reaction area of the lead foam electrode [33]. This protective layer is formed when Pb^{2+} ions under the PbSO_4 film combine with OH^- electrolyzed from water to form tetragonal lead oxide ($\alpha\text{-PbO}$), by a process which is also called stable passivation of lead [34]. The peak potentials of the two kinds of collectors were basically close, but the peak current of the lead-foam collector was almost three times that of the conventional lead cast-grid one, which indicates that more reactions occurred on the lead foam collector making it better than the conventional lead cast-grid collector.

Peak A_3 corresponds to the oxidation of PbSO_4 to PbO_2 and the evolution of O_2 . The oxidation of PbSO_4 generates $\alpha\text{-PbO}_2$ initially, which then transforms into $\beta\text{-PbO}_2$, which is more stable in sulfuric acid [35]. The peak current of lead-foam electrode was almost 80 mA as compared to 2 mA of the cast-grid electrode at a scan rate of 20 mV s^{-1} . This implies that the amount of conductive $\beta\text{-PbO}_2$ generated in the cast-grid electrode was relatively lower, and that at high potentials the lead-foam electrode collector can help the lead-acid battery generate high currents in short time.

In the lead-foam electrode, during the cathodic scan, peak C_1 corresponds to the reduction of PbO_2 to PbSO_4 [36]. This process was accompanied by a large increase of the molar volume of the surface layer. As a result, the sulfate layer cracked, exposing the bare metallic lead to the H_2SO_4 solution (electrolyte). The small oxidation peak A_2 observed after the main reduction peak C_1 was due to the oxidation of the freshly exposed Pb to PbSO_4 [23]. Peak C_2 corresponds to the reduction of several lead oxides ($\text{PbO} + \text{PbO} \cdot \text{PbSO}_4$) into Pb. Peak C_3 corresponds to the reduction of PbSO_4 into Pb, and peak C_4 corresponds to the evolution of H_2 . Peak A_3 , peak C_1 and C_2 were not scanned clearly in conventional lead cast-grid electrode due to the insufficient reaction on the electrode surface. Since the peaks in the voltammograms correspond to the reactions occurring in lead-acid batteries during charge and discharge, the anodic peak A_1 and cathodic peak C_2 correspond to the negative electrode reactions, while the anodic peak A_3 and cathodic peak C_1 correspond to the positive electrode reactions. Therefore, from the voltammograms it can be seen that the oxidation of PbSO_4 to PbO_2 (charge reaction) at the positive electrode occurs above 1.2 V while the peak potentials of the peaks A_1 and C_2 are -1.00 V and -0.93 V, respectively.

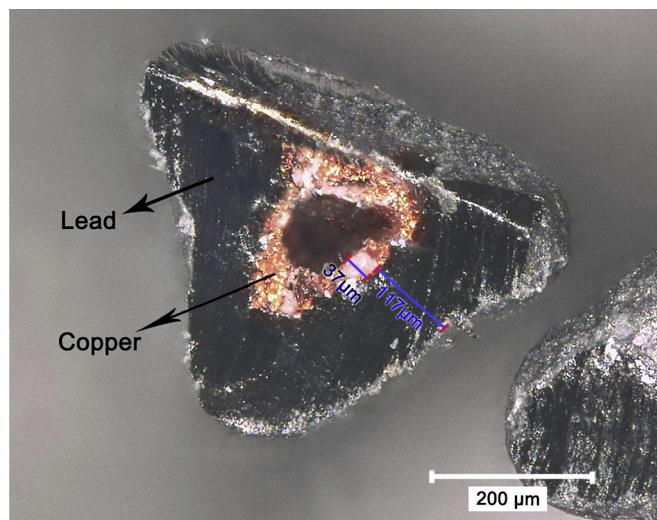


Fig. 5. Optical micrograph of a cross-section of the electroplated lead foam positive current collector.

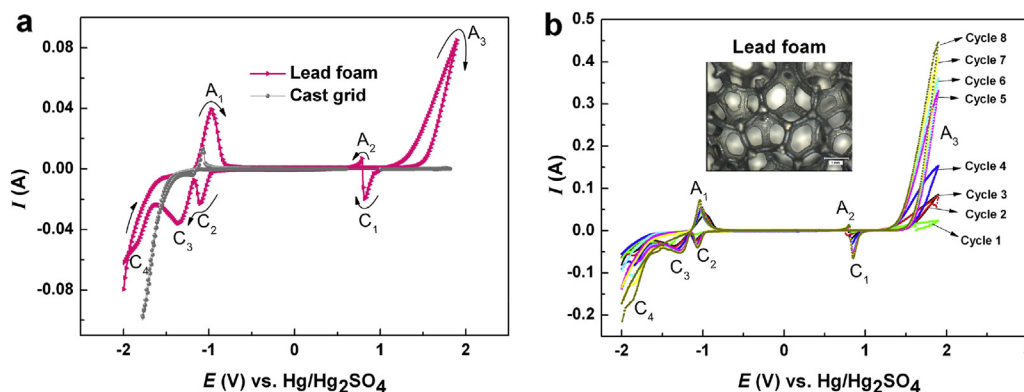


Fig. 6. (a) Single-cyclic voltammograms of the lead-foam (40 PPI) and conventional lead cast grid electrodes. (b) Multi-cyclic voltammetric scan of the lead-foam electrode.

Cyclic voltammograms of 8 cycles of the lead-foam electrode are shown in Fig. 6b. As the number of cycles increased, the peak currents rise due to the accumulation of reactants on the electrodes. However, peak A_3 was not high enough until the fourth cycle because there was not enough PbO_2 formed on the electrode surface. The oxidation and reduction peak potentials were slightly offset to the cathodic and anodic scan directions respectively, which indicates that the electrochemical polarization reduced gradually as the cycle performance of the electrode became stable. After the eighth cycle the lead-foam electrode was removed from the electrolyte at the peak A_3 . And SEM and energy dispersive x-ray spectroscopy (EDS) analysis were carried out on the lead-foam electrode as shown in Fig. 7. The electrode surface was covered with a dense film of PbO_2 . The conductive PbO_2 film generated at high current had a rough surface composed of a mixture of α - and β -phases. And it can have larger contact area and lower contact resistance with the active material.

After electrochemical testing, the concentration of copper ions in the acid solution was monitored by means of flame atomic absorption spectrometry. No leaching of copper ions through the pores of the lead coating and into the sulfuric acid was observed. In addition, there was no visible shedding of lead from the lead-foam electrodes during the electrochemical cycling. The leaching of copper ions from the lead coating into the sulfuric acid solution (in the case of an incomplete lead coating) was probably hampered by the positive standard potential of the electrode in the aqueous acid electrolyte solutions (standard electrode potentials: Cu^{2+}/Cu 0.337 V > Pb^{2+}/Pb -0.126 V). Thus, it can be concluded that the lead coating had a protective effect on the copper-foam substrate when

lead foam was used as the positive current collector. Moreover, the 3D networked structure of the lead foam enabled it to have a greater specific surface area than the 2D conventional cast grid, which meant a larger contact area with the active materials; and the copper-foam substrate in the lead foam not only reduced the weight of the electrode but also improved its conductivity, which transpired into the high peak that was observed during cyclic voltammetry. These are advantages towards improving the utilization efficiency of the active material in the positive electrode of a lead-acid battery.

3.3. Effect of lead foam on the charge/discharge performance of the lead acid batteries

To compare the performance of the lead-foam grids with that of the conventional lead cast grid in lead acid batteries, the charge/discharge properties of the batteries having these electrodes were investigated.

Fig. 8a and b show the charging curves of the different batteries at constant charging currents of 0.5 A and 2 A, respectively. It can be seen that during the initial stages of charging, the voltage rose rapidly at first and then decreased to a point A, followed by slow rise along the curve AB for about 3 h. When the charging time reaches point C, the voltage increases rapidly to reach point D, which corresponds to the electrolysis of water at a stable voltage of 2.8 V. The battery voltage is strongly dependent on the concentration of sulfuric acid. In the initial stage of charging, the active material PbSO_4 in the electrodes was transformed into PbO_2 in the positive electrode and spongy Pb in the negative electrode. The

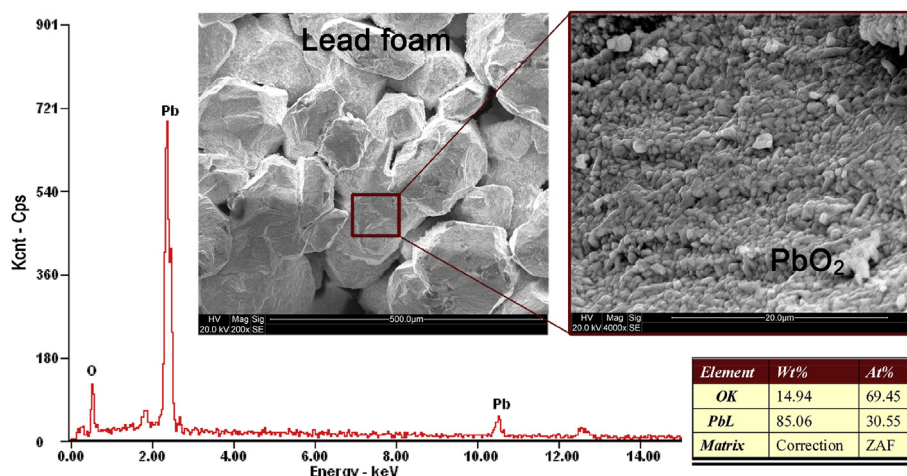


Fig. 7. SEM and EDS analysis of the lead-foam electrode at the peak A_3 after the eighth cycle.

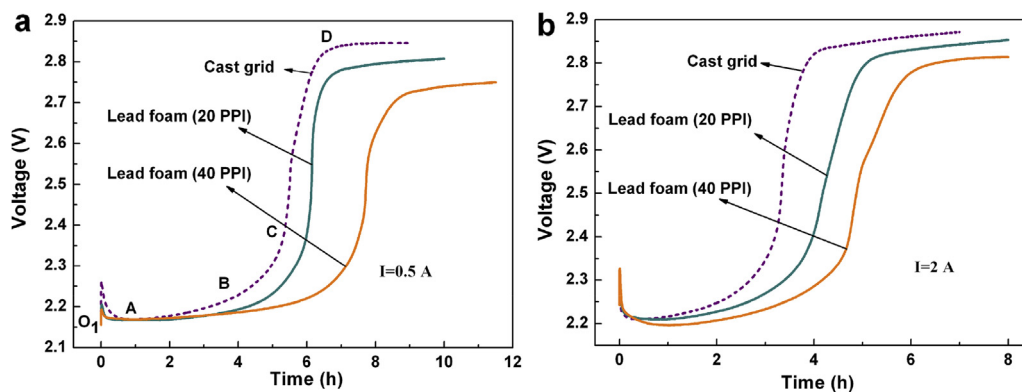


Fig. 8. Charging curves of different batteries at constant charging currents of (a) 0.5 A and (b) 2 A.

charging process was accompanied by the generation of sulfuric acid, which resulted in the rapid increase of sulfuric-acid concentration near the active material causing the voltage to rise. However, due to diffusion the concentration of sulfuric acid in/near the electrode was reduced resulting in a slight voltage drop. Later the concentration of sulfuric acid increased slowly as the charging proceeded, which led to a slow upward rise of the voltage along the curve AB. As the reaction of active material continued, the voids in the electrode also increased gradually. The charging reaction ceased when the amount of PbSO_4 became insufficient, which resulted in a sharp increase of polarization as can be observed by the rise of voltage along the curve CD. Finally, the excess power due to charging was used to decompose water, causing the evolution of O_2 at the positive electrode and H_2 at the negative electrode, and the voltage to stabilize at a fixed value.

The initial charging voltages of the different batteries were close to each other. However, when charging at a constant current of 0.5 A, the lead-foam batteries showed a lower charge voltage than the cast grid ones after they were charged for 2 h, and this gap widened as the charging time progressed (Fig. 8a). However, when charging at 2 A, the charge voltages of the lead-foam batteries diverged from that of lead grid one after 1 h and stayed lower throughout the charging time (Fig. 8b).

Since the hydrogen evolution reaction in the lead-foam batteries occurred at a later time than in the cast grid battery, the lead-foam batteries could be charged with a larger amount of electricity at the same charge voltage. On comparison, it appears that charge voltage of the 40-PPI lead-foam battery was lower than that of the 20-PPI battery, and the hydrogen evolution reaction occurred later too. Therefore, the lead-foam battery, especially the foam having a larger pore density, can be charged by a larger quantity of electricity at the same charge voltage.

Fig. 9 shows the discharge curves of different batteries at different discharge rates. It can be seen from Fig. 9a that there is a “voltage lip” marked by O_2E at the beginning of the discharge process for both lead-foam batteries and cast-grid battery. This can be explained by the dissolution/precipitation mechanism, which is based on the idea that the surface of PbO_2 is progressively reduced to Pb^{2+} during discharging and the Pb^{2+} then goes into the solution [37]. The precipitation of PbSO_4 crystals caused by super-saturation of Pb^{2+} directly affects the polarization of electrode. As the PbSO_4 crystals start to grow, the polarization decreases gradually and so does the discharge voltage. Subsequently, a discharge voltage plateau appears when the electrochemical process reaches equilibrium (EF), which is considered as the discharge voltage of battery. Finally, with the gradual increase of PbSO_4 from PbO_2 and spongy Pb in active materials, the internal resistance rises. This leads to a sharp decline of battery voltage shown by the G point, progressing quickly towards the termination voltage.

The discharge voltages of lead-foam batteries were higher than that of the cast-grid one, which means the lead-foam batteries have a lower internal resistance. Moreover, the discharge voltage and time of 40-PPI lead-foam battery were higher and longer than those of the 20-PPI lead-foam battery at all the rates (20 h, 10 h, 5 h, and 2 h). Because at the same apparent volume, the 40-PPI lead foam can be filled with more active materials than 20-PPI one, and also the 40-PPI lead foam has a greater specific surface area, which is more critical and leads to improved utilization of the active material.

A test battery composed of one lead-foam positive and two cast-grid negative electrodes is also subjected to long-term cycling. Fig. 10 shows the curve of discharge voltage of the 40-PPI lead-foam battery as a function of cycling at 2 h discharge rate and 2 A charge current. The total duration of one charge–discharge cycle was about 8 h. At cycle No. 50 the average discharge voltage was about 20 mV lower than for cycle No. 5, while for the 110th cycle the average discharge voltage was about 2 V but approximately 50 mV lower than for cycle No. 5. After the 110th cycle, the cycling test is continuing until the copper layer in the lead foam is corroded along with the reducing of the lead thickness (Fig. 11).

A sufficient thickness of the lead coating is essential for the lead-foam positive electrode, and it can protect the copper-foam substrate against damage by electrolyte penetration or leaching of copper. The thickness of the lead coating decreases along with the increase of cycling times owing to the development of the corrosion layer influenced by the polarization potential, electrolyte concentration and polarization time (Fig. 11a, b and c). For instance, the thickness ratio of lead layer to copper layer is about 3:1 for the initial sample, compared to 1:1 after 110 charge/discharge cycles. Fig. 11d and e show the surface and cross-section of the lead-foam positive electrode after 110 cycles. It is indicated that the metallic skeleton is well enveloped by PAM and the copper layer as a part of the current collector of the electrode is effectively protected. When the lead layer is corroded to an extent, the acid can immerse random gaps or holes into a copper layer (Fig. 11g), then anode oxidation and corrosion of copper layer occur. Fig. 11f shows the surface topography of the corroded electrode. The traces of corrosion extended on the surface of electrode are composed of some metal oxides. The mechanical strength and electrical conductivity of the lead foam will be weakened and eventual failure due to the corrosion.

The utilization efficiencies of the PAM of different batteries at different discharge rates are shown in Fig. 12a. It is clear that the utilization efficiencies decrease as the discharge rates decrease. This is because the discharge rate has a great influence on the utilization of active material. Smaller discharge rates, lead to larger discharge current densities but uneven current distribution. Currents are preferentially distributed on the surface of the electrode, which is closest to the electrolyte; therefore, PbSO_4 is generated

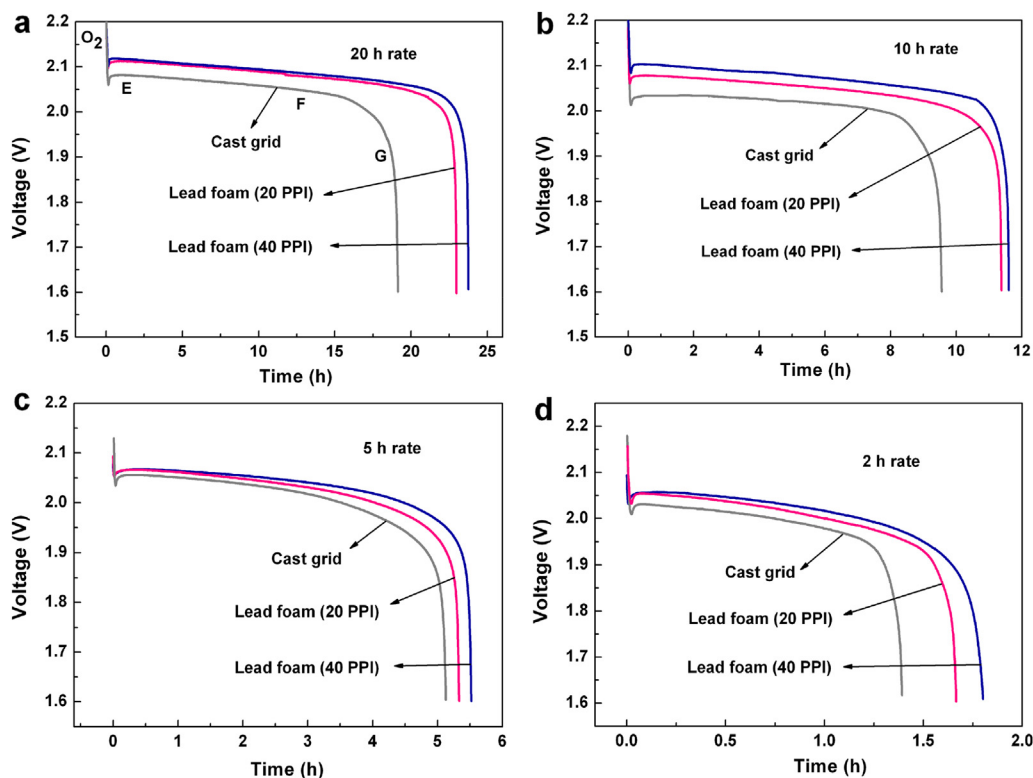


Fig. 9. Discharge curves of different batteries at: (a) 20 h, (b) 10 h, (c) 5 h, and (d) 2 h rates.

initially at the outer surface of the electrode. PbSO_4 has a larger molar volume than PbO_2 and Pb , so they are prone to clogging the pore space of the active material inhibiting the penetration of the electrolyte into the electrode. Thus, the utilization efficiency of the active material was reduced as the discharge current density increased. Compared to the conventional cast-grid battery, the utilization efficiencies of the PAM of lead-foam batteries at different discharge rates were improved, and with a larger the pore density, the utilization of the active material was greater. At the 20 h, 10 h, 5 h, and 2 h discharge rates, the utilization efficiencies of the PAM of 40-PPI lead-foam battery were improved by 19%, 32%, 36%, and 33% respectively, from the cast-grid battery.

The utilization efficiencies of the PAM of 40-PPI lead-foam battery and the conventional cast-grid one as a function of

cycling numbers at 2 h discharge rate are also studied (Fig. 12b). The tendency of PAM utilization of the 40-PPI lead-foam battery changes correspondingly in agreement with that of the cast-grid one along the cycling. The maximum PAM utilization is almost 50% for 40-PPI lead foam when about 44% for cast grid. It can be seen that the PAM utilization starts to degrade from about the 80th cycle for the softening and shedding of PAM. Because the PAM utilization rises along with increased discharge time, this result is comparable to the maximum PAM utilization of 47% at 5 h discharge rate for the carbon honeycomb grid mentioned by Kirchev et al. [8], and 48% at 3 h discharge rate for the electroplated reticulated vitreous carbon current collectors mentioned by Gyenge et al. [24].

The 3D networked structure of the lead foam in the electrode can reduce the density of the current passing through the contact surface, the polarization resistance, and the ohmic resistance because lead foam has a larger contact area with the active material. As a result, the corresponding battery had a higher discharge voltage and utilization efficiency. Therefore, the lead foam can effectively improve the discharge performance of batteries.

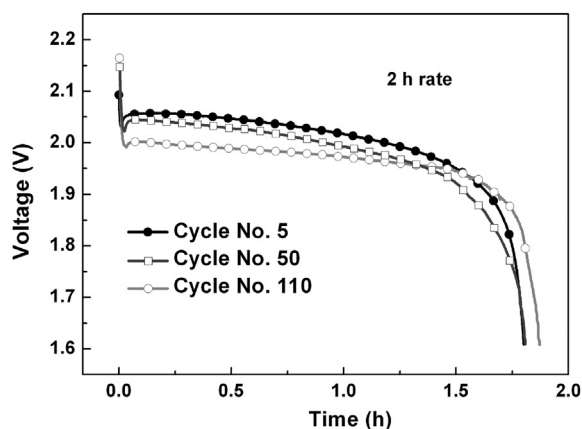


Fig. 10. The curve of discharge voltage of the 40 PPI lead-foam battery with different cycling numbers at 2 h discharge rate.

3.4. Lead-foam model and electrical and mechanical analysis

To build a unit model of the lead foam based on its morphology and synthesis mechanism, we considered a sphere-centered tetrakaidecahedron structure derived from the precursor PU foam. This tetrakaidecahedron has 8 regular hexagons and 6 squares, and it accurately models the frothing process of PU (Fig. 13a) as follows: an air bubble is generated due to the melting of the PU matrix, as the bubble grows up gradually it reaches an equilibrium or a minimum surface energy status, finally it forms a sphere-centered approximate tetrakaidecahedron structure after being solidified. The modeling parameters based on this frothing process basically

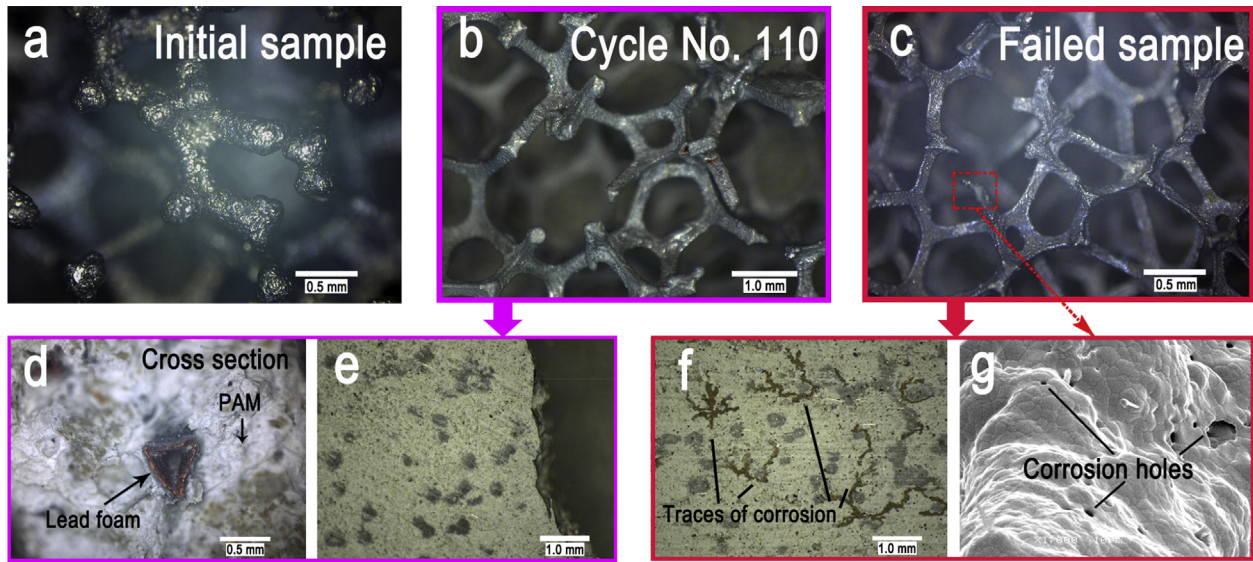


Fig. 11. The morphology of the lead foam and the lead-foam positive electrode under the cycling test (a: the initial lead foam sample, b: the 110th-cycle sample, c: the failed sample, d: the surface of the lead-foam positive electrode after 110 cycles, e: the cross-section of the electrode after 110 cycles, f: the surface of the corroded electrode, and g: gaps or holes on the corroded lead foam).

contain two variables: one representing the edge length of tetra-kaidecahedron (m), and the other representing the radius of the sphere-shaped air bubble (r). The robustness of frothing (air bubble intersects with every surface of tetrakaidecahedron, but keeps the edge of every surface intact), can be determined from the relationship between m and r is as follows:

$$\sqrt{2} < \frac{r}{m} < \frac{3}{2} \quad (1)$$

Based on the principle of minimum surface energy during foaming process, $r/m = 3/2$

The surface density of foamed unit is calculated as follows:

$$\alpha_A = \left[\left(\sqrt{3}\pi + \frac{3}{2}\pi \right) \times \frac{r}{m} - \frac{3\sqrt{2}}{2}\pi \times \left(\frac{r}{m} \right)^2 \right] / m \quad (2)$$

From the length of the edges of the tetrakaidecahedron $m = 0.2$ mm (40 PPI), the surface density of the lead foam can be obtained as follows:

$$\alpha_A = 6.85 \text{ (mm}^2 \text{ mm}^{-3}\text{)} \text{ (40 PPI).}$$

The unit model of the conventional grid lead electrode is shown in Fig. 13b, whose density α'_A can be calculated as follows:

$$\alpha'_A = \frac{A'}{V'_F} = \frac{2\pi dm'}{dm'^2} = \frac{2\pi}{m'} \quad (3)$$

Here, the value of $m' = 2.8$ mm was substituted into formula (3) to get $\alpha'_A = 2.24 \text{ (mm}^2 \text{ mm}^{-3}\text{)}$.

Thus, the surface density of the 40-PPI lead foam was three times larger than the cast grid. Considering the rough surface of lead foam made by electrodeposition (average size of the lead particles = 50 μm), the actual surface area of lead-foam collector may be an order of magnitude greater than that of the conventional one. This ensures that the lead foam has a larger contact area with the embedded active material.

In order to understand the influence of metallic skeletons on the performance of the batteries, the electric field intensity of the lead-foam electrode was simulated by finite element analysis (FEA).

Fig. 13c shows the FEA of the electric field intensity on a lead-foam electrode. Assuming that a current of 0.1 A travels through a square cross section of the lead foam, the distribution of the electric

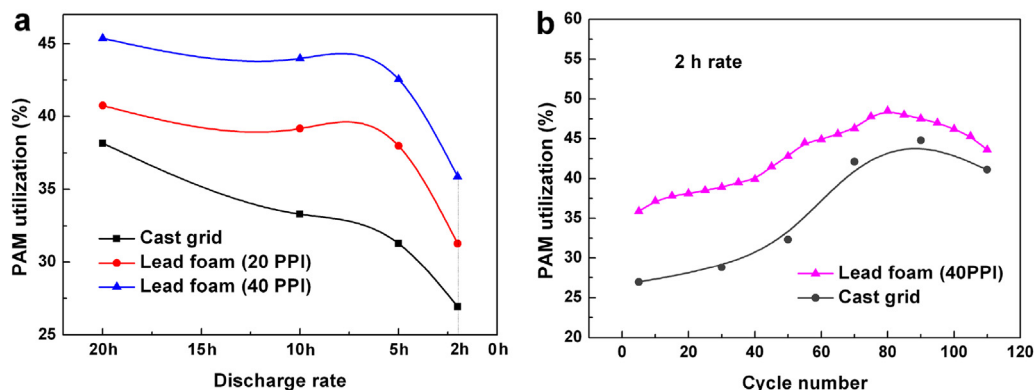


Fig. 12. The utilization efficiencies of the PAM of different batteries as a function of different discharge rates (a) and cycling numbers (b).

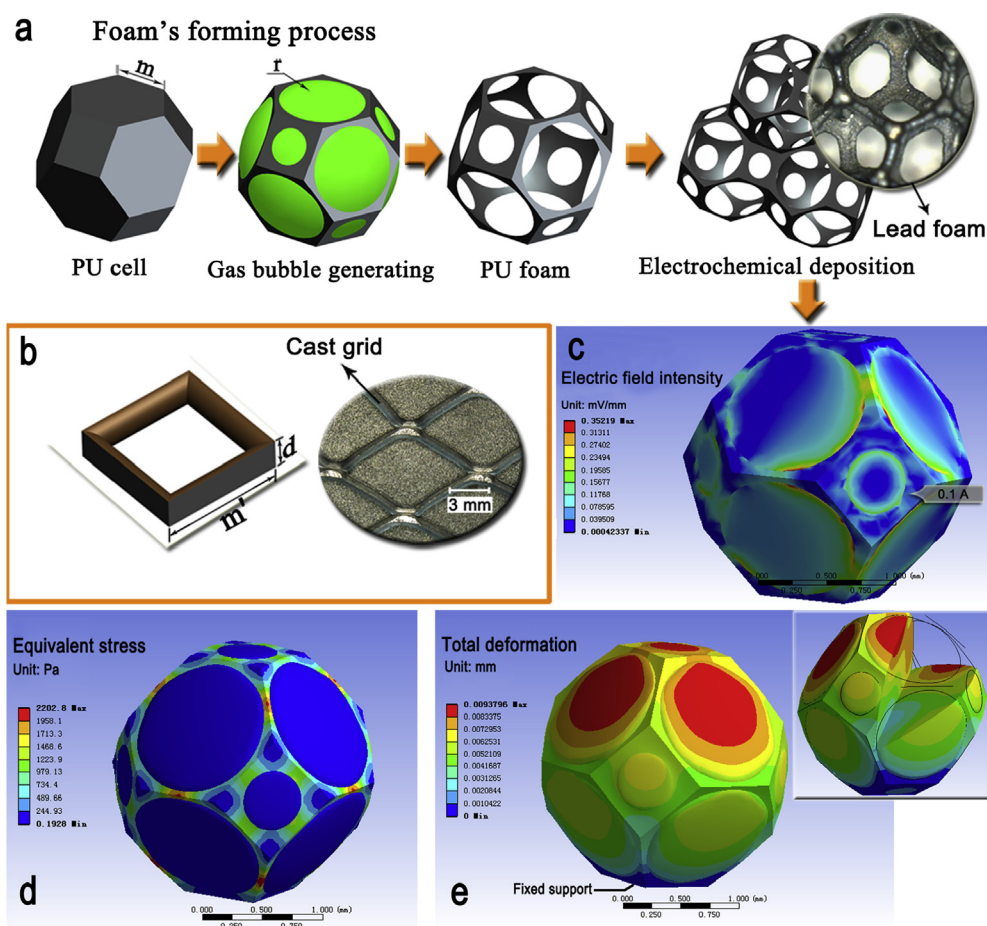


Fig. 13. Unit body modeling of the lead foam grid (a), and conventional lead grid (b), and the FEA of the electric field intensity (c), equivalent stress (d), and total deformation (e) based on the lead-foam model.

field along the current collector adopts a radial profile on the active material. The simulated image reflects the influence of the metallic skeleton on the gradient of the electric field intensity in the active material. With the 3D networked structure, the contact area with the active material increased and the polarization resistance of the electrode decreased.

Due to the thermoelectric effect, PAM in charge/discharge process is prone to expanding and spalling. Under this defect in the cast grid of 2D structure became obvious under deep cycling. In order to better understand the mechanical role of 3D skeleton structure of metal foams on PAM, the model was simulated through the thermal-structure couple. Fig. 13d and e respectively show the equivalent stress distribution and total deformation based on the lead-foam model. It can be seen from Fig. 13d that because of the difference in coefficient of expansion, the PAM unit is surrounded and fastened by the lead-foam unit when PAM is expanding, and a further expansion of PAM especially in the contact area can be suppressed. Fig. 13e shows the deformation of the model unit. A reference surface is given the fixed support. It can be seen that the expansion behavior of PAM is indeed suppressed by the foam-metal skeleton. The farther away from the metallic skeleton is, the more obvious expansion. It also indirectly shows the weakness of 2D cast grid in suppressing expansion of PAM. Therefore, the 3D networked structure could hold the active material more tightly and also slow down the shedding rate, which in turn effectively improves the utilization efficiencies of the PAM and the cycle life of the battery.

4. Conclusions

- (1) A uniform and dense coating of lead was electrodeposited on a copper-foam substrate to fabricate positive current collectors of a lead-acid battery. The electrodeposited lead coating had a thickness of about 117 μm , a uniform coverage, and a good contact with the copper-foam substrate. A lead coating thickness of at least three times the thickness of the copper layer is strong enough to protect the copper-foam substrate against electrolyte penetration. Further, the positive standard potential of the electrode can mitigate the oxidization process of copper in aqueous solutions of acids.
- (2) Cyclic voltammetry indicated that more electrochemical reactions occurred on the lead-foam collector than in the cast lead one. The 3D networked structure of the lead foam enabled it to have a greater specific surface area than the 2D conventional cast grid structure, and the copper-foam substrate of the lead foam improved the conductivity of the electrode, which corroborated with the in higher peak currents observed during the cyclic voltammetry tests. This is advantageous in improving the utilization efficiency of the active material and getting high currents in short time.
- (3) The charge voltages of the lead-foam batteries were lower, while their discharge voltages were higher than that of the cast grid one. The discharge voltage and time of the 40-PPI lead-foam battery were higher and longer than those of the 20-PPI lead-foam battery at different discharge rates. This is

because of the larger pore density, specific surface area, and contact area of the 40-PPI lead foams, which in turn reduced the current density, the polarization resistance, and the ohmic resistance of their batteries. At different discharge rates, the utilization efficiencies of PAM of 40-PPI lead-foam battery were improved by 19%–36% respectively over the cast-grid battery. Moreover, simulation studies show that the 3D networked structure can hold the active material more tightly and also slow down the shedding rate of active materials.

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